UCRL-MA-133867

ES&H manual

Environment, Safety, and Health

Volume II

Part 14: Chemical

14.1 Chemicals

(Formerly H&SM Chapter 21)

Recommended for approval by the ES&H Working Group

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New document or new requirements

Approval date: November 4, 1999
Editorial Update: April 1, 2001

This work performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

14.1

Chemicals*

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1.0 Introduction

This document provides general requirements for the safe use and disposal of hazardous chemicals (generic chemicals; elements; and hazardous chemical products that contain one or more chemicals such as cleaning products, solvents, and lubricants) in laboratories and non-laboratory areas (shop and maintenance and production workplaces). Other documents in the Environment, Safety, and Health (ES&H) Manual contain detailed information about specific chemicals. Requirements for "controlled materials" can be found in Document 21.1, "Acquisition, Receipt, Transportation, and Tracking of Hazardous Materials," in the *ES&H Manual.*

OSHA regulations differentiate between chemical laboratories and non-laboratories. "Laboratory" and "Laboratory use of hazardous chemicals" as used in this document meet OSHA's definition:

> "*Laboratory*" means a facility where the "laboratory use of hazardous chemicals" occurs. It is a workplace where relatively small quantities of hazardous chemicals are used on a non-production basis. At LLNL, this includes chemical, biomedical, and material science laboratories.
>
> "*Laboratory use of hazardous chemicals*" means handling or use of such chemicals in which <u>all</u> of the following conditions are met:
>
> (i) Chemical manipulations are carried out on a "laboratory scale."
>
> (ii) Multiple chemical procedures or chemicals are used.
>
> (iii) The procedures involved are not part of a production process, nor in any way simulate a production process.
>
> (iv) "Protective laboratory practices and equipment" are available and in common use to minimize the potential for worker exposure to hazardous chemicals.

Other laboratories (e.g., laser laboratories) and shops that do not meet all of the requirements of the OSHA definition are <u>*not*</u> considered laboratories in the context of this document.

This document is written for individuals who works with or supervises individuals who use hazardous chemicals in LLNL operations.

2.0 Hazards

Many chemicals are poisonous, irritating, corrosive, carcinogenic, pyrophoric, or explosive (having two or more of these properties is not uncommon). Chemicals that may be relatively safe when used alone can become very dangerous when mixed with other substances, either in a planned experiment or by accident. Therefore, personnel who use, store, dispose of, or transport chemicals shall consider the hazards and use appropriate controls and procedures.

3.0 Controls

Key requirements that apply to both laboratories and non-laboratories are described in the subsections below.

3.1 Planning

The Responsible Individual, Supervisor, or worker shall evaluate the risk(s) associated with each chemical operation. This involves:

- Considering chemical properties and their reactivities and incompatibilities.
- Having the tasks for operations and the chemicals involved reviewed by a Responsible Individual, principal investigator, or supervisor in advance of the operation.
- Establishing disposal options and waste minimization techniques accordingly.

See Document 2.2, "Managing ES&H for LLNL Work," in the *ES&H Manual* to determine whether a safety plan is needed for the chemicals involved in specific operations.

3.2 Chemical Hygiene Plans and Health Hazard Communication

All workers who handle or work around hazardous materials shall be informed of their hazards and be trained in safe handling techniques.

Furthermore, in any work area where hazardous substances are present, there shall be a written plan for identifying and labeling hazards, maintaining collections of material safety data sheets (MSDSs), providing ongoing training on hazard recognition and control, and notifying workers of their rights to obtain safety information. The plan may also include other requirements such as the use of personal protective equipment, medical surveillance, and emergency planning.

These requirements are fulfilled by meeting ISM requirements described in Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," Document 2.2, Document 10.2, "LLNL Health Hazard Communication Program," and Document 14.2, "LLNL Chemical Hygiene Plan for Laboratories," in the *ES&H Manual*. Laboratories meeting the OSHA definition (e.g., chemical, biomedical, material science laboratories) shall follow Document 14.2: all other areas shall follow Document 10.2.

3.3 Chemical Inventories

A complete inventory shall be compiled for non-laboratory areas and updated at least annually. ChemTrack can be used to fulfill this requirement. For the most current requirements, contact your area ES&H Team industrial hygienist or environmental analyst.

To satisfy regulatory requirements for laboratories, a complete inventory of primary (i.e., those shipped by the manufacturer) containers shall be compiled and updated at least annually. Employee responsibilities with regard to chemical inventories are contained in Document 21.1., ChemTrack can be used to fulfill this requirement.

For both laboratory and non-laboratory areas, list hazards by generic categories such as corrosive, flammable, oxidizer, reducing agent, explosive, highly toxic, and reactive on the Health Hazards Communications door signs.

It is recommended that each chemical or product be identified as follows on the inventory:

- List all chemical carcinogens and/or reproductive toxins.
- List each chemical by International Union Pure & Applied Chemistry nomenclature or its trade name, type of container (glass, polyethylene, etc.), chemical grade and quantity. If you have any questions, contact the your area ES&H Team environmental analyst.

The ChemTrack Operations Group at LLNL can provide assistance with chemical inventories, among other things. This group

- Administers and maintains site-wide chemical inventory database of primary chemical containers.
- Conducts an annual site-wide inventory of bar-coded chemical containers.
- Prepares required chemical inventory and use reports for internal customers and regulatory agencies.

- Assists chemical users and Materials Distribution Division personnel with bar-coding and chemical inventory activities upon request.
- Maintains the MSDS Hotline (ext. 4-4404) and the ChemTrack website (http://chemtrack.llnl.gov.1600/) with multiple links to various MSDS internet sites.

3.4 Material Safety Data Sheets

Federal hazard communication laws require chemical manufacturers and importers to prepare MSDSs for their products. Each data sheet provides detailed information about the physical, chemical, and toxicological properties of a particular chemical and recommended controls for handling the material.

Requirements for obtaining MSDSs and making them available to workers in the workplace are different for laboratories and non-laboratories. These requirements are detailed in Document 10.2. "Training course HS4050, "Health Hazard Communication for Supervisors" is available on this subject and shall be taken by Responsible Individuals (RIs) whose workers handle hazardous materials in non-laboratory areas. RIs for laboratories shall take course HS4052, "Health Hazard Communication for Supervisors of Chemical Labs." All employees and contractors may take course HS4050 or HS4052.

If a manufacturer's MSDS lacks the information needed for safe use of the material, the experimenter or the supervisor should call the area ES&H Team for assistance. The manufacturer will be contacted for more information, if required, and a supplemental MSDS may be prepared. When a material of unknown toxicity is developed at LLNL, an MSDS shall be prepared and the container shall be appropriately labeled before the material may be shipped offsite.

3.5 Facilities and Equipment

Adequate facilities, equipment, and protective clothing necessary to control the hazards related to specific chemical operations shall be obtained before beginning work. General requirements for areas using chemicals include the following:

- Install cabinets and shelving in chemical use areas using the tie-down standard developed by the LLNL Plant Engineering Department. Also use restraining devices (e.g., shelf bars, rods) to keep chemical containers on shelves during an earthquake (see Document 22.4, "Earthquakes," in the *ES&H Manual* for details).
- Install an ANSI-approved safety shower and eyewash station (see Document 42.1, "Design and Construction" in the *ES&H Manual* for specifications.

- Use local-exhaust ventilation fume hoods or close-capture systems for any experiment that produces hazardous quantities of gas, vapor, or airborne particulates in the work environment. Such ventilation shall be the "once-through" type that permits no recirculation of exhaust air.
- Cover floors and bench-top surfaces with impermeable materials for easy cleanup of spilled chemicals (see Document 42.1 for details).
- Use safety goggles, face shields, liquid-proof aprons, and gloves when handling containers of corrosive chemicals (see Document 14.8, "Working Safely With Corrosive Chemicals," in the *ES&H Manual*.
- Provide separate containers for uncontaminated broken glass.
- Dispose of used hypodermic syringes by placing them in an appropriate sharps container.

3.6 Chemical Storage

General requirements for chemical storage areas are as follows:

- Provide fresh-air ventilation (e.g., 10 to 15 air changes per hour).
- Install cabinets and shelving for chemical storage areas using the tie-down standard developed by the LLNL Plant Engineering Department. Also use restraining devices (e.g., shelf bars, rods) to keep chemical containers on shelves during an earthquake (see H&SM C27 for details).
- Clearly label the storage area and each container. The container labeling requirements for laboratories and non-laboratories are different. These requirements are outlined in Appendix C. Users shall evaluate hazards, identify proper containers and controls before transferring or dispensing chemicals from manufacturer-supplied chemical containers to secondary containers. The secondary container shall be labeled appropriately. Appendix A provides an overview of several labeling formats commonly used. Labels for common chemicals are available from the ES&H Team. The ES&H Team can also assist in obtaining labels for unique chemicals.
- Store incompatible chemicals separately to prevent accidental mixing, as might happen during an earthquake. For example, the following classes of chemicals are mutually incompatible: acids, bases, oxidizers, flammables, toxics, and water reactives. Contact your area ES&H Team for information about specific chemicals and for copies of the storage precaution signs in Appendix B.

- Provide secondary containment to hold spills (e.g., trays), particularly for liquids in glass containers.
- Limit quantities of materials in storage and in use to the minimum necessary (see Section 3.10 for details). Provide adequate storage space and containers, and observe the shelf-life limits for chemicals—particularly peroxides and peroxidizable materials (see Section 3.8 for details).

  A visual inspection of stored chemicals is important in the continued storage or disposal decision. Indications for disposal of chemicals are

  — Slightly cloudy liquids.
  — Change in color of chemicals.
  — Spotting on solid chemicals.
  — Caking of anhydrous materials that is evidence of reaction with moisture.
  — Presence of precipitates or particulates in liquids, or liquid in solids.
  — Pressure buildup in bottle (bulging of container).
  — Container damage (signs of cracking, changing shape or color).

  Call the Fire Department, 911, if there is any evidence of bulging, overpressurization, peroxidation, or any other reaction that could potentially make handling the container hazardous.
- See Document 22.5, "Fire," in the *ES&H Manual* for the storage requirements for flammable liquids.
- Store chlorinated hydrocarbons such as trichloroethylene, methylene chloride, 1,1,1-trichloroethane, and perchloroethylene (tetrachloroethylene) in special containers as specified below to minimize environmental pollution.

  — Areas that use small amounts of chlorinated solvents should store them indoors in relatively small containers as required by this document.
  — Use of 55-gal drums is not recommended; use of refillable safety cans is preferred. However, areas that must use 55-gal drums of chlorinated solvents shall store them in a facility that has the following characteristics:

  1. Is dry, well ventilated, completely covered, and lighted (a shed with openings for light and air would suffice).
  2. Is designed so that spills drain to a holding area (pan, berm, etc.) that is leakproof, holds 55 gal, and is protected from rain.
  3. Allows storage of drums in a *vertical* position.

4. Uses a drum transfer pump with a drip-return pan or equivalent (e.g, a Protectoseal Model H4500N available from California Safety and Supply Co., Santa Clara, CA).

5. Has an entrance easily accessible by manual drum-handling devices.

   An alternative to constructing this facility is to store 55-gal drums in existing buildings that meet the same requirements. The 55-gal-capacity, spill-containment requirement can be waived in this case, as long as the building is regularly occupied and no floor drain to the sanitary sewer exists in the storage room. Approved storage cabinets (e.g., Protectoseal Models 5555 (one drum) and 555W (two drums), or equivalent) shall be used. These cabinets are not designed for outside use and do not provide the 55-gal spill containment required for outdoor storage.

- Every chemical storage area shall have a person designated to inspect the area and assure good maintenance. Storage areas shall be inspected at least annually, looking for problem indicators, out-of-date chemicals, or those that are no longer used. Chemicals that are no longer needed can be recycled through CHEW, if it is safe to do so. A phone number of the Responsible Individual should be posted.

Plant Engineering has experience in designing facilities to meet the above requirements. Contact your Plant Engineering field team for more information.

3.7 Handling Solid and Liquid Chemicals

Chemicals whose toxicity and chemical and physical properties have not been fully characterized or studied, including newly synthesized chemicals, should be considered hazardous. Therefore, only use a small quantity of such materials to minimize the effects of unexpected reactions. In addition to this, observe the following safety precautions:

- Keep the work area clean and orderly.
- Do not eat, drink, smoke, apply cosmetics, or store food in the work area.
- Read all container labels and the MSDSs if they are available.
- Use required safety equipment. The minimum protective clothing is a laboratory coat and safety glasses; for additional protection, wear gloves and a face shield. (See Document 11.1, "Personal Protective Equipment," in the *ES&H* for additional information.)

- Isolate hazardous operations in separate rooms; limit the number of personnel involved.
- Whenever possible, select chemicals that are the least hazardous.
- Use mechanical aids for all pipetting procedures (e.g., pipette with rubber bulb).
- Limit the volume of volatile or flammable materials to the amount required for daily operations.
- Users shall evaluate hazards, identify proper containers and controls before transferring or dispensing chemicals from manufacturer-supplied chemical containers. The secondary container shall be labeled appropriately. (See Section 3.6, third bullet.)
- Provide secondary containment for holding spills.
- Provide safe, conveniently located sinks and hand cleaners. (Do not use solvents.)
- If the operating system is used under pressure or can generate pressure, follow the requirements in Document 18.1, "Pressure," in the *ES&H Manual*.

3.8 Peroxidizable Materials

IMPORTANT: Workers shall implement the requirements in *Standard for Storing and Using Peroxidizable Organic Chemicals,* UCRL-AR-133218, while beginning work with peroxides or peroxidizable materials. (This UCRL will be converted to a Document at some time in the future.)

Peroxidizable materials form unstable peroxides when they are in the presence of oxygen, stored for long periods of time, or exposed to sunlight. These materials may explode when disturbed, when the caps are removed from their containers, or when the chemicals are used. Peroxides may also be formed even if preservatives or inhibitors are added to slow down the peroxidization process. Thus, these chemicals should be protected from exposure to light, heat, and air.

In addition, peroxides should be stored in accordance with the time limitations specified in Table 1. Old containers of peroxide-forming chemicals that are improperly stored are most likely to be dangerous, especially if discoloration, crystallization, or layering is observed. If there is reason to believe that dangerous levels of peroxides may be present in a container, immediately contact the Fire Department (dial 911). The Fire Department will handle the chemical until it is determined that it is not an imminent hazard.

Table 1. Common chemicals that form explosive levels of peroxides and their storage limits.[a]

Peroxidizable chemicals		
High hazard - autopolymerizes (24 hr–12 month storage)[c,d]	**Medium hazard - may become heat or shock sensitive 'on the shelf' (3-month storage)**	**Potentially hazardous - may form heat or shock sensitive residue on evaporation or distillation[b,c] (12-month storage)**
Acrylic acid	Butadiene[d,e]	Acetal
Acrylonitrile[e,f]	Chloroprene[f]	Acetaldehyde
Butadiene[e,g]	Divinyl acetylene	Benzyl alcohol
Chloroprene	Isopropyl ether	2-Butanol
Chlorotrifluoroethylene	Potassium metal	Cyclohexanol
Methyl methacrylate	Sodium amide	2-Cyclohexene-1-ol
Styrene	Tetrafluoroethylene[f]	Cumene
Tetrafluoroethylene	Vinylidene chloride	Decahydronaphthalene
Vinyl acetate		Diacetylene
Vinyl acetylene		Dicyclopentadiene
Vinyl chloride[e]		Diethyl ether
Vinyl pyridine		Diethylene glycol dimethyl ether
		Dioxanes
		Ethylene glycol dimethyl ether
		4-Heptanol
		Methyl acetylene
		Methyl isobutyl ketone
		3-Methyl-1-butanol
		Methylcyclopentane
		2-Pentanol
		4-Pentene-1-ol
		1-Phenylethanol
		2-Phenylethanol
		2-Propanol
		Tetrahydrofuran
		Tetrahydronaphthalene
		Vinyl ethers
		Other secondary alcohols

a Other materials than those listed may form peroxides. Contact your ES&H Team for further information.
b May become unstable if concentrated by the user.
c Chemicals to be stored for 24 hours if uninhibited or 12 months if inhibited.
d When stored as an inhibited liquid monomer.
e OSHA-related carcinogen.
f When stored as a liquid monomer.
g When stored as a gas.

3.9 Handling Gases

Considerable care should be used in handling compressed or liquefied gases. When released into the work environment, toxic gases may be inhaled or corrosive gases may come in contact with unprotected human tissue. Workers who work with gases should be familiar with their properties and their reaction with the human body. In addition, gases may be corrosive, flammable, or explosively reactive when they come in contact with other chemicals, toxic or radioactive, (e.g., ^{3}H) as the following examples illustrate:

- In low concentrations, chlorine is corrosive to metals as well as to human tissue.
- Acetylene is incompatible with silver, mercury, and copper and, under certain conditions, may react explosively with any of them.
- Nickel carbonyl is very toxic, even at low concentrations.

Because gases are usually supplied in cylinders under pressure, workers working with these materials should be familiar with Document18.1. For detailed information on specific gases, especially those that are toxic, refer to the following sources:

- Document 14.3, "Toxic, Corrosive, or Reactive Gases," in the *ES&H Manual*.
- *Matheson Gas Data Book* and *Fire Protection Guide on Hazardous Materials* (National Fire Protection Association).
- Area ES&H Team.

3.10 Waste Minimization

Waste minimization is important because it helps protect the environment while also reducing the cost and administrative difficulties associated with disposing of hazardous wastes. Waste minimization means limiting inventories and the use of hazardous materials to quantities as small as possible. This also improves safety wherever hazardous materials are stored and used.

Waste minimization begins when planning *any* experiment or job. Plan to use the smallest vessels, apparatus, or equipment that is practical and safe for a given task. Also develop or improve and implement new procedures and techniques that will generate less waste. Try to eliminate or minimize generating "surplus waste." Choose equipment, procedures and techniques that (1) use the least hazardous material available, (2) use the smallest quantities of hazardous materials, (3) generate the least amount of hazardous waste, and (4) are practical and safe for any given task.

Other key elements of hazardous waste minimization are

- *Share inventories* of hazardous chemicals with other users in the area. This reduces duplication of hazardous materials and hazardous waste generation because the entire group can maintain a reserve rather than each member having his/her own. This means that fewer containers will reach the end of their shelf lives or be discarded when a particular user no longer needs a specific hazardous material.
- *Reuse* hazardous materials whenever possible. Select procedures and equipment that allow hazardous materials to be reused whenever this is practical and safe. For example, mineral acids used to clean the new glassware can be reused several times before being disposed of.
- *Transfer your surplus hazardous materials*, if possible, to others in the Laboratory who can use them before you dispose of them.

The Chemical Exchange Warehouse (CHEW), operated by the Hazardous Waste Management Division, was established in October 1993 to reduce hazardous waste generated at LLNL. CHEW collects, sorts, and temporarily stores unused, surplus chemicals and advertises their availability to other users (both onsite and offsite). CHEW supplies the excess chemicals free-of-charge to LLNL requestors. The benefits of waste minimization are two-fold: the chemical recipients can reuse the excess chemicals from another program, and the chemical donors do not have to pay for the waste disposal.

- *Hazardous materials should be disposed of promptly* at the end of their shelf lives. Test hazardous materials that have reached their shelf-life limits (1) to determine that they are still useful if you still need the material, and (2) whenever such retesting is practical. Supervisors/principal investigators, building managers, and building coordinators shall not allow unlabeled containers or cylinders to accumulate. Personnel moving out of a lab or shop shall either dispose of hazardous materials as hazardous waste before leaving or transfer unused or partially used hazardous materials to others.
- Waste generators shall identify the hazardous materials to be disposed of as required by LLNL's Waste Acceptance Criteria (WAC) and other requirements identified in the *ES&H Manual*. It is usually expensive and time consuming to analyze an unknown material to determine its chemical and radiological composition. The Waste Acceptance Criteria's web-site is at http://www.llnl.gov/llnl_only/es_and-h/wac_rev1/wac_contents.html

Contact the area ES&H Team environmental analyst regarding any questions you may have on implementing waste minimization ideas.

3.11 Chemical Waste Disposal

Waste chemicals and spent chemical solutions produced by LLNL operations can pose a threat to the environment if they are not properly managed. Such wastes shall be disposed of by Hazardous Waste Management. Before disposing of any chemicals, contact your area ES&H Team environmental analyst or hazardous waste technician for guidance on proper packaging, labeling, and storage requirements (see the WAC and Document 36.1, "Waste Management Requirements," in the *ES&H Manual*.

Hazardous waste generators and waste handlers shall attend training presented by the Environmental Protection Department (course EP0006, "Hazardous Waste Generation and Certification").

3.12 Chemical Spills

Detailed information about spills of specific chemicals can be found in Document 22.2, "Environmental Emergency Response," in the *ES&H Manual*. Small spills of materials normally handled in a given area can usually be cleaned up safely by the workers involved; however, they shall be trained in advance to handle cleanups.

Environmental regulations and DOE orders have reporting requirements for chemical spills above certain amounts or when there is a potential for harm to individuals, property, or the environment. Report all spills of hazardous chemicals to the area ES&H Team health and safety technician and environmental analyst.

If the spill is too large to clean up safely or if workers have been injured or contaminated, immediately call the Laboratory emergency number (911). The LLNL Fire Department operates a HAZMAT (hazardous material) truck to respond to major spills.

4.0 Responsibilities

Listed below each title are the responsibilities of individuals who work with hazardous materials. All workers and organizations shall refer to Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," in the *ES&H Manual* for a list of general responsibilities. This section describes specific responsibilities of LLNL organizations and workers who have key safety roles.

4.1 Responsible Individual /Principal Investigator/Work Supervisor

- Establish safe procedures.
- Enforce LLNL, state, and federal regulations.

- Provide the protective equipment and clothing needed in handling chemicals.
- Instruct personnel about the possible hazards, safety precautions, waste handling, and actions necessary during normal operations and in case of an accident.
- Ensure that workers are held accountable for the chemicals they work with. In case of a job transfer or termination, workers shall properly dispose of or transfer all chemicals to another responsible party before leaving.

4.2 Workers

- Be familiar with the properties of the chemicals you work with; follow all safety procedures.
- In cases of malfunction or damage or if injury occurs, protect yourself and others in the area.
- Report any unsafe or hazardous condition in the area to your supervisor and the ES&H Team.

4.3 The Hazards Control Department

- Through the ES&H Teams, assist supervisors and workers in maintaining safe work areas by providing information on the hazardous properties of materials and relevant regulations.
- Recommend methods for controlling and monitoring the work environment.
- Maintains a set of current Work Smart Standards.
- Offer formal education and training courses. See Document 40.2, "Environment, Safety, and Health Training and Education," in the *ES&H Manual* for safety courses on chemical hazards.
- Maintain all monitoring results and make this information available to RIs and the Health Services Department.

4.4 Environmental Protection Department

- Conduct a hazard review to evaluate environmental contamination problems, permit requirements, NEPA declarations, and other environmental issues during the experimental design phase.
- Ensure environmental compliance through environmental monitoring and risk assessment and analysis.

- Assist LLNL programs with developing environmentally sound practices and with meeting regulatory requirements in their day-to-day tasks.
- Develop and conduct cost-effective restoration and remediation methodologies, technologies, and processes.
- Design and apply appropriate cost-effective treatment technologies and strategies for the management of waste streams.
- Identify waste minimization and pollution prevention opportunities.
- Offer environmental training courses to the LLNL workers.

4.5 Health Services Department

The Health Services Department provides services covered in Document 10.1, "Occupational Medical Program," in the *ES&H Manual.* The following services relate to chemicals:

- Medical Treatment Services for chemical injuries.
- Maintains antidotes and salves, as requested, for emergency response.

5.0 Work Standards

29 CFR 1910.94, *Ventilation.*

29 CFR 1910.107, *Spray Finishing using Flammable and Combustible Materials.*

29 CFR 1910.108, *Dip Tanks Containing Flammable or Combustible Liquids.*

29 CFR 1910, Subpart I, *Personal Protective Equipment.*

29 CFR 1910, Subpart K, *Medical and First Aid.*

29 CFR 1910, Subpart Z, *Toxic & Hazardous Substances.*

- For non-laboratories, 29 CFR 1910.1200.
- For laboratories, 29 CFR 1910.1450.

29 CFR 1926.50, *Medical Services and First Aid.*

29 CFR 1926.62, *Lead.*

29 CFR 1926, Subpart Z, *Toxic & Hazardous Substances.*

40 CFR 68.150 - 68.190, *Chemical Accident Prevention Provisions,* "Risk Management Plan."

40 CFR 170, *Worker Protection Standard.*

40 CFR 171, *Certification of Pesticide Applicators.*

40 CFR 260, *Hazardous Waste Management System: General.*

40 CFR 261, *Identification and Listing of Hazardous Waste.*

40 CFR 262, *Standards Applicable to Generators of Hazardous Waste.*

40 CFR 763, Subpart E, *Asbestos Containing Materials in Public Schools.*

ACGIH Industrial Ventilation Manual (current edition).

ACGIH TLVs and BEIs: *Threshold Limit Values for Chemical Substances and Physical Agents*, 1998.

ANSI Z358.1-1990, *American National Standard for Emergency Eyewash and Shower Equipment*. Testing frequency for emergency showers is to be monthly rather than weekly as required by the standards.

ANSI Z9.5-1992, *American National Standard for Laboratory Ventilation* (see Sections 5.7 and 5.8).

ANSI Z49.1-1994, *Safety in Welding, Cutting, and Allied Processes.*

ANSI Z88.2-1992, *American National Standard for Respiratory Protection.*

Book of SEMI Standards

Standard F4-1990, "Guide for Remotely Actuated Cylinder Valves."

Standard F6-1992, "Guide for Secondary Containment of Hazardous Gas Piping Systems."

Standard F13-1993, "Guide for Gas Source Control Equipment."

Standard F14-1993, "Guide for Gas Source Equipment Enclosures."

Standard S2-1993, "Safety Guidelines for Semiconductor Manufacturing Equipment."

Standard S5-1993, "Safety Guidelines for Flow Limiting Devices."

Compressed Gas Association (CGA)

Pamphlet P-1, S*afe Handling of Compressed Gases in Containers*, 1991.

Pamphlet P-12, *Safe Handling of Cryogenic Liquids*, 1993.

Pamphlet S-1.1, *Pressure Relief Device Standards*, Part 1 "Cylinders for Compressed Gases," 1995.

Pamphlet S-1.2, *Pressure Relief Device Standards*, Part 2, "Cargo and Portable Tanks for Compressed Gases," 1995.

Pamphlet S-1.3, *Pressure Relief Device Standards, Part 3* "Compressed Gas Storage Containers," 1995.

Department of the Army Pamphlet 40-8, O*ccupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Nerve Agents GA, GB, GD, and VX* (12/4/90).

Department of the Army Pamphlet 40-173, *Occupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Mustard Agents H, HD and HT* (8/30/91).

DOE N 440.1, "Interim Chronic Beryllium Disease Prevention Program."

HEPA Filter and In-place Leak Testing Standard, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR-133354.

NFPA 45, *Standard on Fire Protection for Laboratories using chemicals* (1996 edition).

Fire Protection Guide on Hazardous Materials (National Fire Protection Association).

6.0 Resources for More Information.

6.1 Contacts

See the ES&H Contact list.

6.2 Applicable Lessons Learned.

6.3 Other Sources

ASHRAE Handbook of Fundamentals, Chapter 15, "Airflow Around Buildings," (1997).

Book of SEMI Standards, Standard F3-1994, "Guide for Welding Stainless Steel Tubing for Semiconductor Manufacturing Operations."

DOE Order 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees," Attachment 2, "Contractor Requirement Document," Sections 1-11, 13-18 (delete item 18.a), 19 (delete item 19.d.3) and 22.

Safety in Academic Chemistry Laboratories, a publication of the American Chemical Society Committee on Chemical Safety, ISBN 0-8412-1763-7, 5th edition, 1990.

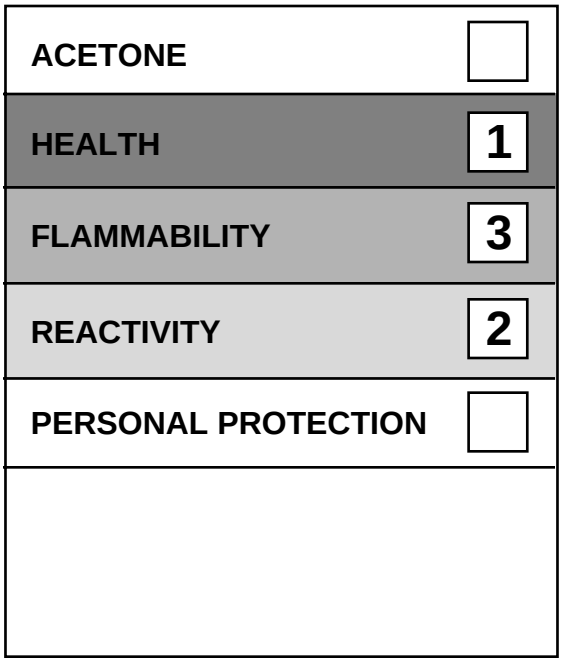
Standard for Storing and Using Peroxidizable Organic Chemicals, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR- 133218.

Appendix A

Labeling Formats for Chemical Containers

(Also See Appendix C)

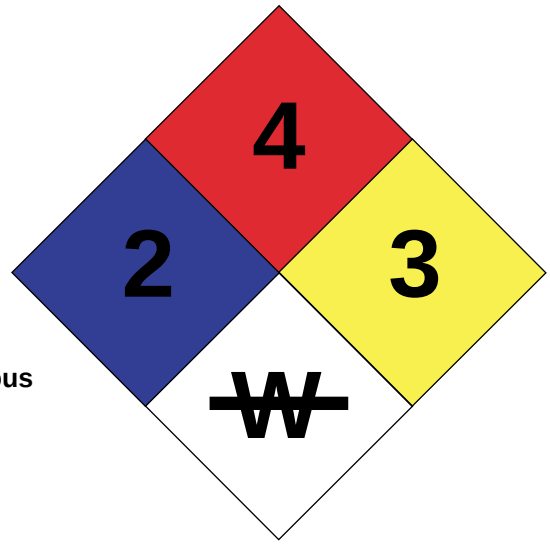
HMIS—Hazardous Material Identification System, a labeling system developed by the National Paint and Coatings Association that uses letters, numbers, and symbols to communicate hazard information. The following example explains how to read the label. Note: These labels do not meet the OSHA requirements for labeling chemical containers in non-laboratories.



4	Severe hazard
3	Serious hazard
2	Moderate hazard
1	Slight hazard
0	Minimal hazard

Figure A-1. Hazardous Material Identification System.

NFPA—National Fire Protection Association. The NFPA developed a diamond-shaped label with numbers and symbols to communicate hazard information about chemicals. The following example explains how to read the label. Note: These labels do not meet the OSHA requirements for labeling chemical containers in non-laboratories.



(red)
Fire hazard

Flash points:
4 Below 73°F
3 Below 100°F
2 Above 100°F, not exceeding 200°F
1 Above 200°F
0 Will not burn

(blue)
Health hazard

4 Deadly
3 Extreme danger
2 Hazards
1 Slightly hazardous
0 Normal material

(yellow)
Reactivity

4 May detonate
3 Shock and heat may detonate
2 Violent chemical change
1 Unstable if heated
0 Stable

(white)
Specific hazard

Oxidizer	**OX**
Acid	**ACID**
Alkali	**ALK**
Corrosive	**COR**
Use NO WATER	W
Radioactive	

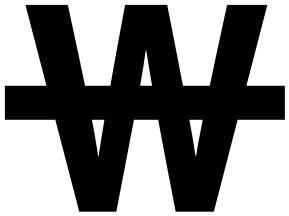
Figure A-2. National Fire Protection Association.

Appendix B

Storage Precaution Signs for Hazardous Chemicals

Copies of the storage precaution signs shown in Figs. B-1, Water Reactive Chemicals;, B-2, Oxidizers; B-3, Pyrophoric Substances; B-4, Toxic Compounds; B-5, Flammables; and B-6, Acids and Bases can be obtained from your ES&H team. These signs should be posted in areas where hazardous chemicals are used.

WATER REACTIVE CHEMICALS



Storage Precautions:

- **Store in a cool, dry place.**
- **In case of fire, keep water away.**

WARNING: These chemicals react with water to yield flammable or toxic gases or other hazardous conditions.

Solids

Aluminum choride, anhydrous
Calcium carbide
Calcium oxide
Ferrous sulfide
* Lithium
Magnesium
Maleic anhydride
Phosphorous pentachloride
Phosphorous pentasulfide
* Potassium
* Sodium

* Lithium, potassium, and sodium should be stored under kerosene or mineral oil.

Liquids

Acetyl chloride
Chlorosulfonic acid
Phosphorous trichloride
Silicon tetrachloride
Stannic chloride
Sulfur chloride
Sulfuryl chloride
Thionyl chloride

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Figure B-1. Water Reactive Chemicals.

OXIDIZERS

Storage Precautions:

- **Store in a cool, dry place.**
- **Keep away from flammable and combustible materials (such as paper, wood, etc.).**
- **Keep away from reducing agents such as zinc, alkaline metals, and formic acid.**

Solids

Ammonium dichromate	Nitrates, salts of [4]
Ammonium perchlorate	Periodic acid
Ammonium persulfate	Permangic acid
Benzoyl peroxide	Peroxides, salts of [5]
Bromates, salts of [1]	Potassium dichromate
Calcium hypochlorite	Potassium ferricyanide
Cerric sulfate	Potassium permanganate
Chlorates, salts of [2]	Potassium persulfate
Chromium trioxide	Sodium bismuthate
Ferric trioxide	Sodium chlorite
Ferric chloride	Sodium dichromate
Iodates, salts of [3]	Sodium nitrite
Iodine	Sodium perborate
Magnesium perchlorate	Sulfates, salts of [6]
Manganese dioxide	

[1] Potassium bromate, sodium bromate, etc.
[2] Potassium chlorate, etc.
[3] Sodium iodate, etc.
[4] Ammonium nitrate, ferric nitrate, etc.
[5] Lithium peroxide, sodium peroxide, etc.
[6] Ferric sulfate, potassium sulfate, etc.

Liquids

Bromine	Nitric acid
Chromic acid	Perchloric acid
Hydrogen peroxide	Sulfuric acid

Gases

Chlorine	Nitrogen oxide
Chlorine dioxide	Oxygen
Fluorine	Ozone
Nitrogen dioxide	

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Figure B-2. Oxidizers.

PYROPHORIC SUBSTANCES

Storage Precaution:

- **Store in a cool, dry place.**

WARNING: Pyrophoric substances ignite spontaneously upon contact with air.

Boron	* Iron
* Cadmium	* Lead
* Calcium	* Manganese
* Chromium	* Nickel
* Cobalt	† Phosphorous, yellow
Diborane	* Titanium
Dichloroborane	* Zinc
2-Furaldehyde	

* Finely divided metals form a pyrophoric hazard.

† Phosphorous, yellow, should be stored and cut under water.

LIGHT-SENSITIVE CHEMICALS

Storage Precautions:

- **Avoid exposure to light.**
- **Store in amber bottles in a cool, dry place.**

Bromine	Mercurous nitrate
Ethyl ether	Oleic acid
Ferric ammonium citrate	Potassium ferrocyanide
Hydrobromic acid	Silver salts[2]
Mercuric salts[1]	Sodium iodide

1 Mercuric chloride, mercuric iodide, etc.

2 Silver acetate, silver chloride, etc.

PEROXIDE-FORMING CHEMICALS

Storage Precautions:

- **Store in airtight containers in a dark, cool, and dry place.**
- **Label containers with receiving, opening, and disposal dates.**
- **Dispose of peroxide-forming chemicals before expected date of first peroxide formation in accordance with LLNL policy.**
- **Test for the presence of peroxides periodically.**

WARNING: Under proper conditions, these chemicals will form explosive peroxides that can be detonated by shock or heat.

Acetaldehyde	Ethyl ether
Acrylaldehyde	Isopropyl ether
Crotonaldehyde	* Potassium
Cyclohexene	Tetrahydrofuran
p-Dioxane	

* Potassium peroxide often exists in the crust around a chunk of potassium. When cut with a knife, the peroxide rapidly oxidizes the residual kerosene, resulting in an explosion.

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Figure B-3. Pyrophoric Substances.

FLAMMABLES

Storage Precautions:

- **Store in approved safety cans or cabinets.**
- **Segregate from oxidizing acids and oxidizers.**
- **Keep away from any source of ignition: flames, localized heat, or sparks.**
- **Safety cans or drums containing flammable liquids should be grounded and bonded when being used.**
- **Keep firefighting equipment readily available.**
- **Have spill cleanup materials handy.**
- **Store highly volatile flammable liquids in a specially equipped refrigerator.**

Solids

Benzoyl peroxide
Calcium carbide
Phosphorous, yellow
Picric acid

Liquids

Acetaldehyde
Acetone
Acetyl chloride
Allyl alcohol
Allyl chloride
N-amyl acetate
N-amyl alcohol
Benzene
N-butyl acetate
N-butyl alcohol
N-butylamine
Carbon disulfide
Chlorobenzene
Cyclohexane
Diethylamine
Diethyl carbonate
p-Dioxane
Ethanol
Ethyl acetate
Ethyl acrylate
Ethylamine
Ethyl benzene
Ethylene dichloride
Ethyl ether
Ethyl formate
Furan
Gasoline
Heptane
Hexane
Hydrazine
Isobutyl alcohol
Isopropyl acetate
Isopropyl alcohol
Isopropyl ether
Mesityl oxide
Methanol
Methyl acetate
Methyl acrylate
Methylal
Methyl butyl ketone
Methyl ethyl ketone
Methyl formate
Methyl isobutyl ketone
Methyl methacrylate
Methyl propyl ketone
Morpholine
Naphtha
* Nitromethane
Octane
Piperidine
Propanol
Propyl acetate
Propylene oxide
Pyridine
Styrene
Tetrahydrofuran
Toluene
Turpentine
Vinyl acetate
Xylene

Gases

Acetylene
Ammonia
Butane
Carbon monoxide
Ethane
Ethyl chloride
Ethylene
Ethylene oxide
Formaldehyde
Hydrogen
Hydrogen sulfide
Methane
Propane
Propylene

* Most nitrohydrocarbons are flammable.

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Figure B-4. Flammables.

TOXIC COMPOUNDS

Storage Precaution:

- **Store according to hazardous nature of chemical, using appropriate security when necessary.**

WARNING: These chemicals are dangerous or extremely dangerous to health and life when inhaled, swallowed, or absorbed by skin contact. Take proper precautionary measures to avoid exposure.

Solids

Antimony compounds
Arsenic compounds
Barium compounds
Beryllium
Cadmium compounds
Calcium oxide
Chromates, salts of
Cyanides, salts of
Fluorides, salts of
Iodine
Lead compounds
Mercuric compounds
Oxalic acid
Phenol
Phosphorous, yellow
Phosphorous pentachloride
Phosphorous pentasulfide
Picric acid
Potassium
Selenium compounds
Silver nitrate
Sodium hydroxide
Sodium hypochlorite

Liquids

Aniline
Bromine
Carbon disulfide
Carbon tetrachloride
Chloroform
Chromic acid
p-Dioxane
Ethylene glycol
Formic acid
Hydrazine
Hydrobromic acid
Hydrochloric acid
Hydrofluoric acid
Hydrogen peroxide
Mercury
Nitric acid
Perchloric acid
Phosphorous trichloride
Sulfuric acid
Tetrachloroethane
Tetrachloroethylene

Gases

Carbon monoxide
Chlorine
Cyanogen
Diborane
Fluorine
Formaldehyde
Hydrogen bromide
Hydrogen chloride
Hydrogen cyanide
Hydrogen sulfide
Nitrogen dioxide
Ozone
Sulfur dioxide

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Figure B-5. Toxic Compounds.

ACIDS

Storage Precautions:

- **Store in large bottles of acids on low shelf or in acid cabinets.**
- **Segregate oxidizing acids from organic acids and flammable and combustible materials.**
- **Segregate acids from bases and active metals, such as sodium, potassium, magnesium, etc.**
- **Segregate acids from chemicals that could generate toxic gases upon contact, such as sodium cyanide, iron sulfide, etc.**
- **Use bottle carriers for transporting acid bottles.**
- **Have Spill Control Pillows or acid neutralizers available in case of acid spills.**

* Acetic acid
* Benzoic acid
* Chloroacetic acid
† Chromic acid
† Hydrobromic acid
Hydrobromous acid
Hydrochloric acid
Hydrochlorous acid
Hydrofluoric acid
Hydroiodic acid
† Iodic acid
Muriatic acid
† Nitric acid
Nitrous acid
† Perchloric acid
* Phenol
Phosphoric acid
Phosphorous acid
* Propionic acid
* Sulfamic acid
* Sulfanilic acid
† Sulfuric acid
Sulfurous acid

* Indicates organic acids.
† Indicates strong oxidizing acids.

BASES

Storage Precautions:

- **Segregate bases from acids.**
- **Store solutions of inorganic hydroxides in polyethylene containers.**
- **Have Spill Control Pillows or caustic neutralizers available for caustic spills.**

Ammonium hydroxide
Bicarbonates, salts of[1]
Carbonates, salts of[2]
Calcium hydroxide
Potassium hydroxide
Sodium hydroxide

[1] Potassium bicarbonate, sodium bicarbonate, etc.
[2] Calcium carbonate, sodium carbonate, etc.

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Figure B-6. Flammables.

Appendix C

Labeling Requirements for Chemical Containers

C.1 Container Labeling Requirements for Non-Laboratories

The chemical manufacturer, importer, or distributor is required to ensure that each container of hazardous chemicals is labeled, tagged, or marked with the following information:

- Chemical name,
- Type of hazard and target organ.
- Special precautions.
- Emergency information.
- The name and address of the chemical manufacturer, importer, or other responsible party.

If the chemical is dispensed into another secondary container, that container shall be labeled with the same information. Labels for common chemicals are available from the ES&H Team. The ES&H Team can also assist in obtaining labels for unique chemicals. The MSDS cannot be used as a substitute for a proper label for a chemical in a non-laboratory. However, the MSDS shall be available to the workers in the work area throughout each work shift.

C.2 Container Labeling Requirements for Laboratories

The chemical manufacturer, importer, or distributor is required to ensure that each container of hazardous chemicals is labeled, tagged, or marked with the following information:

- Chemical name,
- Type of hazard and target organ.
- Special precautions.
- Emergency information.
- The name and address of the chemical manufacturer, importer, or other responsible party.

If the chemical is dispensed into another secondary container (including a waste container), that container shall be labeled with the contents.

The MSDS shall be available to the workers in the work area throughout each work shift.